Characterization and Processing of Cottonseed Oil Obtained by Extraction with Supercritical Carbon Dioxide[1]

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ABSTRACT

Extraction of flaked cottonseed with supercritical carbon dioxide at temperatures of 50-80 C and pressures of 8,000-15,000 psi yields an improved crude cottonseed oil compared to those obtained by conventional solvent or expeller processes. Improvements include lighter initial color, less refining loss and lighter refined bleached colors. Crude cottonseed oils obtained by supercritical fluid extraction require less refining lye and show less tendency to undergo color fixation while in storage.

INTRODUCTION

Recently, there has been much interest in the use of supercritical fluid (SCF) for the extraction of oilseeds, and previous reports from this laboratory have described work with soybeans and corn germ (1-3). This report extends the work to cottonseed and details some preliminary observations on the composition, processing and organoleptic properties of oils obtained by extraction of cottonseed flakes with supercritical carbon dioxide (SC-CO_2). Cottonseed oil generally is considered to be more difficult to process than the other common vegetable oils, because it contains somewhat higher levels of free fatty acids and is more intensely colored as the result of the presence of gossypol and related pigments that are carried along during solvent extraction or expeller pressing.

EXPERIMENTAL

The apparatus used for SCF extractions was that described previously (2). Dehulled cottonseed (8.6% moisture) was passed through cracking and flaking rolls to yield flakes 0.007 inches thick. The flaked cottonseed (1,600 g) was charged into an alloy steel autoclave and extracted as described previously (2,3). After removal from the receiving vessel, the crude oil was slurried with Filter-cel®, and the mixture was filtered through a bed of Celite® under vacuum. Analysis for iron, free fatty acids, neutral oil, phosphorus, unsaponifiable matter, gossypol and color were conducted by official AOCS methods as described previously (2). Tocopherol was determined according to AOAC method 43-092 (4).

Refining, bleaching and deodorizing were carried out as described previously (5). Representative samples of commercial crude prepress-solvent and expeller crude cottonseed oils used for comparative studies were obtained from reliable sources. Color fixation was determined by refining the crude oil at 25 C according to the method of Pohle et al. (6) and determining the refined color. Samples (4 oz) of the crude were then placed in wide-mouthed jars and stored at 40 C and 60 C in a forced-draft oven for varying lengths of time, followed by refining and color determination. The increase in red color after refining was taken as the extent of color fixation that occurred during storage. Organoleptic evaluations were carried out as described previously (7).

RESULTS AND DISCUSSION

The effects of temperature and pressure on the solubility of triglycerides have been reported (8). The present report will deal with these parameters only as they related to crude and finished oil quality. Flaked cottonseed was extracted with SC-CO_2 at 8,000-15,000 psi and at temperatures ranging from 50 to 80 C, to yield 30.5% oil ±0.4% with <1% residual oil remaining in the defatted meal. The resulting crude cottonseed oils were characterized, and the results are shown in Table I. Included for comparison are commercial samples extracted by the traditional prepress-solvent and expeller extraction methods.

Free fatty acids (FFA) are quite soluble in SC-CO_2. The FFA content of crude cottonseed oil extracted under the conditions shown is slightly higher than in the commercially processed samples examined. However, the FFA content of crude cottonseed oil is known to vary with the climatic conditions under which the seed is grown (9). Thus, the FFA content of SC-CO_2-extracted cottonseed will depend on the condition of the seed and would be expected to parallel that of hexane or expeller pressed oil from the same seeds.

Phosphatides show very low solubility in SC-CO_2. Compared to the large amounts of phosphorus in expeller- and solvent-processed oil, crude cottonseed oil obtained from seed extracted with SC-CO_2 contains only trace amounts. In preliminary work with a low capacity CO_2 compressor, which required extraction times of up to 16-18 hr, oils contained up to several hundred ppm phosphorus. However, with a high capacity compressor and under the conditions reported in Table I, the extraction times were shorter (7-8 hr) and phosphorus levels of only 1-59 ppm were observed. Phosphorus contents of expeller- and solvent-extracted oils of 386 and 674 ppm equate to about 1 and 1.7% phosphatides (% P × 25.5), respectively. These values are in line with reported literature values (1). The phosphorus levels of SC-CO_2-extracted oils usually are so low (<5 ppm) as to imply that phosphatides are virtually absent.

The absence of phosphatide in SC-CO_2-extracted crude cottonseed oil accounted for the lower neutral oil losses compared to expeller- and solvent-processed oils.

Total unsaponifiable matter in SC-CO_2-extracted crude cottonseed oil is slightly lower but comparable to expeller and prepress-solvent crudes. Total unsaponifiables for cottonseed oil reportedly range from 0.5-7% (9). Tocopherol contents of CO_2-extracted crude are somewhat lower than of commercially extracted oils.

Commercially extracted crude cottonseed oils are extremely dark because of their gossypol and related pigment content. Typically these oils are so dark that color cannot be measured at the standard height of 5¼ inches in the Lovibond color test because they exceed 20 red units and must be measured for color at a 1-inch depth. Crude CO_2-extracted cottonseed oils are markedly lighter in color than solvent or expeller oils and may be analyzed at the full depth in the Lovibond sample tubes.

Crude cottonseed oil contains up to 0.21% gossypol, depending on the extent of heat treatment of the seed prior to extracting or expelling (1). The solvent-prepress and expeller oils (Table I) contained 0.18 and .085% gossypol, respectively. The gossypol content of CO_2-extracted oils typically is about .02% under the most stringent extraction conditions, i.e., 80 C and 15,000.

The effects of processing on the color of hexane-extracted

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TABLE I

Effect of CO_2 Extraction Conditions on Crude Cottonseed Oil Quality and Minor Constituents

Oil	CO_2 extraction Temp. C	CO_2 extraction Press. psi	Lovibond color Y	Lovibond color R[a]	FFA %	Phos. ppm	Ref. loss[b] %	Excess Alkali, %	Neutral oil, % loss	Iron ppm	Unsaps %	Tocopherol %	Gossypol %
Prepress solvent	–	–	70	20(1")	1.15	664	6.7	0.5	3.4	1.8	0.87	0.092	0.18
Expeller	–	–	70	20(1")	0.92	386	3.6	0.5	3.6	1.9	0.76	0.095	0.085
CO_2	50	8,000	70	8(5¼")	1.3	1	1.8	0.2	1.8	0.2	0.51	0.072	0.015
CO_2	50	15,000	70	12(5¼")	1.3	1	1.8	0.2	1.8	0.2	0.53	0.046	0.016
CO_2	80	8,000	70	7(5¼")	1.7	1	1.7	0.2	1.7	0.2	0.52	0.053	0.019
CO_2	80	15,000	70	>20(5¼")	1.4	59	1.7	0.2	1.7	0.6	0.52	0.053	0.021

[a]Value in parentheses is the cell depth.
[b]Refined with 10% NaOH–Pohle et al. (6). Losses are centrifugal losses, % excess alkali is that over amount needed to neutralize FFA.

TABLE II

Effects of Processing on Cottonseed Oil Color[a]

Oil type	Lovibond color[b] Crude Y	Crude R	Refined, % Excess alkali	Refined Y	Refined R	Bleached Y	Bleached R	Deodorized Y	Deodorized R	Flavor score[c] O, Time	Flavor score[c] 4-Day, 60 C
Hexane (Prepress solvent)	70	20	0.5	70	8	70	4	20	2.5	7.9	7.7
Hexane (Prepress solvent)	70	20	0.3	70	16	20	9	20	5.0	8.2	6.4
Hexane (Prepress solvent)	70	20	0.2	70	20	20	16	20	6.0	8.1	7.4
CO_2[d]	70	7.6	0.1	70	3.5	30	2	20	1.0	7.6	7.1

[a]Refining steps ref.: 10% lye; bleached with 0.5% activated clay, 80 C; vac. 15 min; deodorized, 3 hr at 210 C.
[b]Prepress solvent (hexane) crude oils at 1", all others 5¼".
[c]10 Point scale; 10 = bland, 1 = extreme.
[d]Composite oil extracted 40-80 C, 8,000-15,000 psi.

cottonseed oil at various stages of processing are shown in Table II. Included are typical comparative data for CO_2-extracted cottonseed oil. According to the literature, cottonseed oil is refined with a sufficient excess of caustic to give the desired color consistent with a low refining loss (6). Refined, bleached and deodorized cottonseed oils typically range from 4 to 7 red units in color compared to 1.0-2.5 red units for shortening stocks (9). In order to achieve acceptable color (2.5-6 R) in refined, bleached and deodorized products, hexane-extracted oil required 0.2 to 0.5% excess of 10% lye, whereas the CO_2 oil required only 0.1-0.2% excess of the same lye.

Processing of crude cottonseed oil presents a problem known as color fixation (9,10). Solvent-extracted and expeller-pressed oils contain appreciable amounts of pigments that, upon heating, become difficult or impossible to remove by refining and/or bleaching. The low solubility of cottonseed pigment in SC-CO_2 suggested that oils extracted in this way would show less tendency to undergo color fixation than conventionally extracted oils. Preliminary experiments (Fig. 1) indeed showed that oils extracted with CO_2 at low temperatures and pressures, i.e., 50 C and 8,000 psi, showed no tendency to undergo color fixation when stored at 40 C. At 60 C the rate of color fixation was about half that of an expeller crude oil. Thus, extraction of cottonseed with SC-CO_2 at low temperatures and pressures obviates the problem of color fixation. Further work is in progress and will be reported later.

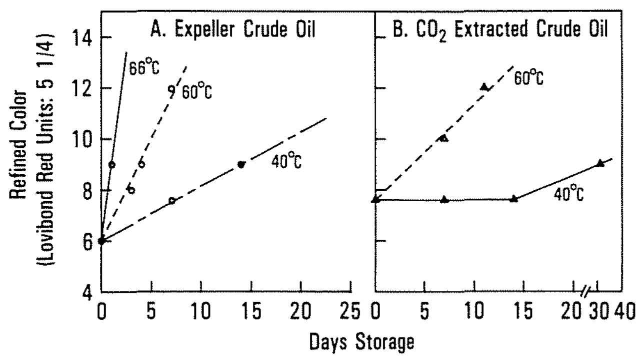

FIG. 1. Color fixation in expeller- and CO_2-extracted cottonseed oils: (A) expeller oil refined with 10% lye, 0.5% excess; (B) CO_2-extracted oils (extracted 70-80 C, 12,000 psi) refined with 10% lye, 0.2% excess.

Preliminary work reported here indicates that extraction of cottonseed with SC-CO_2 yields crude oil that is lighter in color, shows low refining losses, requires less caustic soda for color reduction and is resistant to color fixation.

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REFERENCES

1. Friedrich, J.P., and G.R. List, J. Agric. Food Chem. 30:192 (1982).
2. Friedrich, J.P.; G.R. List and A.J. Heakin, JAOCS 59:288 (1982).
3. Christianson, D.D.; J.P. Friedrich, G.R. List, K. Warner, A.C. Stringfellow, E.B. Bagley and G.E. Inglett, J. Food Sci. 49:229 (1984).
4. Official Methods of Analysis, (1980), 13th edn., p. 754. AOAC, Arlington, VA.
5. List, G.R.; T.L. Mounts, K. Warner and A.J. Heakin, JAOCS 55:277 (1978).
6. Pohle, W.D.; R.L. Gregory and S.E. Tierney, JAOCS 40:703 (1963).
7. Moser, H.A.; H.J. Dutton, C.D. Evans and J. Cowan, Food Technol. 4:105 (1950).
8. Friedrich, J.P., U.S. Patent Application 06/364,240.
9. Bailey, A.E., Cottonseed and Cottonseed Products. Their Chemistry and Chemical Technology, Interscience Publishers, Inc., New York (1948).
10. Vix, H.L.E.; E.F. Pollard, J.J. Spadaro and A. Gastrock, Ind. Eng. Chem. 38:635 (1946).

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